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1495457

PATENT SPECIFICATION

(11) **1 495 457**

(21) Application No. 9315/75 (22) Filed 6 March 1975
(23) Complete Specification filed 5 March 1976
(44) Complete Specification published 21 Dec. 1977
(51) INT CL² C08L 47/00, 61/08
(52) Index at acceptance
C3P 2D1A1 E2 PC13A PC13C PC14A PC17 PC2 PC8B
T2D T2X
C3R 1C C11 C12 C14A C16 C25 C33B C4 C6A1 C6B
C6X C8B C8P C8R L2X L6G
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(19)

ERRATUM

SPECIFICATION No. 1,495,457

Page 1, line 1, (71), *after We, insert THE*
THE PATENT OFFICE
20th February, 1978

20 among the paints which have recently been proposed for electropainting are those based on the completely or partly neutralised reaction products obtained by reacting a polydiene resin with an α,β -ethylenically unsaturated dicarboxylic acid component, for example maleic anhydride or itaconic anhydride or their half-esters, in admixture with another resin, particularly a phenol formaldehyde resin. The term "polydiene resin" is used herein to denote a linear homopolymer of a diene, for example, butadiene, isoprene or chloroprene, or a linear copolymer of a major molar proportion of a diene with a minor molar proportion of one or more other ethylenically unsaturated compounds, for example styrene, acrylonitrile or an α -olefin. The maleinised or like polydiene resin of the prior art may be used in its anhydride form, in its hydrolysed form, in the form of its mono-
30 amide, or in the form of its half-ester obtained by esterification with the required amount of
35 4 to 30% of its weight of an α,β -ethylenically unsaturated dicarboxylic acid, suitably of 4 to 5 carbon atoms, for example maleic acid, fumaric acid, itaconic acid or a mixture of two or more thereof, or
40 (ii) the reaction product of (i) which has been partially esterified with an alcohol containing 1 to 4 carbon atoms in the molecule, or
45 (iii) the reaction product of a polydiene resin, as defined above, with from 4 to 30% of its weight of α,β -ethylenically unsaturated dicarboxylic anhydride, suitably of 4 to 5 carbon atoms, for example maleic anhydride or itaconic anhydride or a mixture thereof, in which the anhydride content of the product has been substantially hydrolysed to the acid, or has been substantially half-
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ALEXANDER BARCLAY



(54) IMPROVED ELECTROPAINTS

(71) We, INTERNATIONAL PAINT COMPANY LIMITED, a British Company of Henrietta House, 9, Henrietta Place, London, W1A 1AD, England, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to electropaints, that is paints which can be applied to metal articles by electrodeposition.

15 With the commercial adoption of electro-painting, a variety of so-called water-soluble paints have been developed based on resinous binders which are acidic in nature and can be taken up in water when they are partially or completely neutralised.

20 Among the paints which have recently been proposed for electro-painting are those based on the completely or partly neutralised reaction products obtained by reacting a polydiene resin with an α,β -ethylenically unsaturated dicarboxylic acid component, for example maleic anhydride or itaconic anhydride or their half-esters, in admixture with another resin, particularly a phenol formaldehyde resin. The term "polydiene resin" is used herein to denote a linear homopolymer of a diene, for example, butadiene, isoprene or chloroprene, or a linear copolymer of a major molar proportion of a diene with a minor molar proportion of one or more other ethylenically unsaturated compounds, for example styrene, acrylonitrile or an α -olefin. The maleinised or like polydiene resin of the prior art may be used in its anhydride form, in its hydrolysed form, in the form of its monoamide, or in the form of its half-ester obtained by esterification with the required amounts of

The present invention provides improved aqueous electropaints based on polydiene resins which have higher rupture voltage figures than previously proposed paints of the same type. In electropainting, the higher the voltage at which the paint can be applied, the higher is the throwing power that can be achieved.

In accordance with the present invention, the binder of an aqueous electropaint is a partially or completely neutralised composition which prior to neutralisation contains at least one of each of the following three essential ingredients A, B and C:

A a polydiene reaction product which is

- (i) the reaction product of a polydiene resin, as defined above, with from 4 to 30% of its weight of an α,β -ethylenically unsaturated dicarboxylic acid, suitably of 4 to 5 carbon atoms, for example maleic acid, fumaric acid, itaconic acid or a mixture of two or more thereof, or
- (ii) the reaction product of (i) which has been partially esterified with an alcohol containing 1 to 4 carbon atoms in the molecule, or
- (iii) the reaction product of a polydiene resin, as defined above, with from 4 to 30% of its weight of α,β -ethylenically unsaturated dicarboxylic anhydride, suitably of 4 to 5 carbon atoms, for example maleic anhydride or itaconic anhydride or a mixture thereof, in which the anhydride content of the product has been substantially hydrolysed to the acid, a has been substantially half

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cule, or has been substantially converted to a monoamide by reaction with ammonia, or a primary or secondary amine;

5 B the reaction product of a polydiene resin, as defined above, with from 4 to 30% of its weight of maleic anhydride or itaconic anhydride; and

10 C a heat-reactive (i.e. thermosetting) phenol-formaldehyde resin,

the acid value of the components A and B in total being at least 30 mg KOH/gram.

15 The preferred polydiene resin in both component A and component B is a homopolymer of butadiene. The homopolymer may be a 1:2 or 1:4 polymer or a mixture of the two. The molecular weight of the homopolymer is not critical and may vary conveniently from 200 to 20,000. As well as homopolymers, copolymers containing a major molar proportion of butadiene with a minor molar proportion of one or more other monomers such as styrene and acrylonitrile may be used.

20 When the polydiene resin is reacted with maleic anhydride in making component A (iii) for further reaction as described, the preferred amount of maleic anhydride used is from 15 to 30 *per cent* by weight, relative to the polydiene resin. In component B, however, the amount of maleic anhydride used is preferably lower and the preferred range of maleic anhydride in component B is not more than 12 *per cent*, particularly from 5 to 10 *per cent* and possibly at least 6 *per cent* by weight, relative to the polydiene resin.

25 Components A and B are preferably present in a weight ratio of from 1:4 to 4:1 and the proportion of the phenolic resin (component C) is preferably from 1 to 25 *per cent* by weight of the total weight of components A and B. Components A and B may be mixed together in the absence of a solvent but generally it is more convenient to form a solution of one component and then to disperse or emulsify the other component in the solution.

30 Examples of suitable solvents are alcohols, ketones, glycol ethers, aliphatic or aromatic hydrocarbons, or polyols. The acid value of the components A and B in total must be at least 30 mg KOH/gram.

35 The phenolic resin (component C) must be a heat-reactive one, that is to say it must be thermosetting. The phenol used may be phenol itself, a cresol, xylenol, bisphenol A or it may also contain a carboxylic acid group as for example salicylic acid; phenols with an unsaturated side chain, e.g. allyl phenol, may also be used. The resin used may be an alcohol-modified phenolic resin, for example

A, B and C, the three components may be mixed in any order. For example, the phenolic resin C may be mixed with component B or may be co-condensed with it before blending the mixture or product with component A.

65 The composition used according to the invention may be based on one each of the components A, B and C. However, more than one of each type of component may be used. For example, we have found that some advantages may be obtained by using two types of component B; in particular, we have successfully used a mixture of components B in which the same butadiene resin has been condensed with different amounts of maleic anhydride or itaconic anhydride.

70 When the components A, B and C have been adequately mixed, the composition is neutralised and dispersed in water, for example by adding an aqueous solution of the neutralising agent. The neutralising agent may for example be ammonia, an amine, an alkanolamine or an alkali metal or alkaline earth metal hydroxide; mixture of neutralising agents may also be used. It is not necessary that the composition should be completely neutralised but it is preferred that at least 50 per cent of the acid groups should be neutralised.

75 80 It is important, particularly in cases where the mixture of components A, B and C contains an alcohol, which may have been used for example, as a solvent, that neutralisation should be carried out as soon as possible otherwise the rupture value of the composition tends to fall.

85 90 The electropaints according to the invention may contain any of the pigments normally used in electropaints, for example titanium dioxide, iron oxide, carbon black, talc, clay and chromates such as strontium chromate. The pigments can conveniently be dispersed in the normal way in one of the components, for example component A. A drier metal such as cobalt, lead, manganese or iron may also be present for example in the form of an oxide, salt or soap, for example as a linoleate or naphthenate.

95 100 105 Other optional additives in the electropaint include the following:

(a) vegetable oils or maleinised vegetable oils;

(b) epoxy resins, epoxy resin esters or maleinised epoxy resins;

(c) styrene/allyl alcohol copolymers, or the esters or maleinised reaction products thereof;

(d) urea-, melamine- or benzoguanamine-formaldehyde resins, which may be partially or completely etherified with a lower alcohol, i.e. one containing 1-4

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These optional additives may be present in proportions of up to 20 per cent by weight based on the total weight of components A, B and C.

5 The invention is illustrated by the following Examples in which parts and percentages are by weight.

Example 1.

10 Component A — Polybutadiene-Maleic Anhydride Half-ester

500 parts of a polybutadiene having a viscosity of 7 poises at 25°C and 100 parts of maleic anhydride were heated together at 200°C for 8 hours. The product was cooled to 100°C and 35 parts of methyl alcohol were added; the temperature was maintained at 70°C for 2 hours so as to form the methyl half-ester. The final product was dissolved in a mixture of 300 parts of diacetone alcohol and 300 parts of n-butyl alcohol.

20 Component B — Maleinised Polybutadiene

500 parts of a polybutadiene having a viscosity of 20 poises at 25°C and 50 parts of maleic anhydride were heated together at 190°C for 6 hours.

25 Component C — Phenolic Resin

450 parts of phenol, 150 parts of paraformaldehyde and 4.5 parts of sodium hydroxide were heated together at 60°C for 2 hours and the temperature was then raised to 90°C over a further 4 hours. The resulting phenol-formaldehyde resin was dissolved in 250 parts of methyl ethyl ketone.

30 Preparation of Electropaint

35 10 parts of titanium dioxide and 20 parts of talc were finely dispersed in 100 parts of component A after which 50 parts of component B and 13 parts of component C were mixed in. The product was immediately dispersed in a solution of 14 parts of triethylamine in 300 parts of water and finally a further 300 parts of water was added to give the required electropaint.

35 Electropainting

40 The electropaint prepared as described above when electropainted on to mild steel was found to have a rupture voltage of 200 volts. The corresponding rupture voltages for similarly-prepared electropaints but without either component A or component B were below 150 volts in both cases.

Example 2.

45 Component A — Hydrolysed Polybutadiene-Maleic Anhydride Product

50 First stage — 100 parts of a polybutadiene of molecular weight 1,000 to 1,500, 3 parts of xylene and 0.3 part of Tropolon M (a

heated together with continuous stirring under an atmosphere of nitrogen in a vessel fitted with a condenser. 6.25 parts of maleic anhydride was added, the temperature raised to 180°C and held for half an hour whereupon a further 6.25 parts of maleic anhydride was added. The temperature was held at 180°C for 3 hours and the product was then allowed to cool.

Second Stage — 0.5 part of triethylamine, 25 parts of water and 30 parts of 4-methylpentan-2-ol were added to the first stage product and the mixture was heated at 100°C for 1 hour in order to hydrolyse the anhydride groups. The alcohol and unreacted water were then removed by passing a vigorous stream of nitrogen through the product.

50 Component B — Polybutadiene-Maleic Anhydride Product

This was prepared as described in the first stage above.

55 Component C — Phenolic Resin

This was the commercially available methylated phenolic resin Methylon 75108 (METHYLON is a Registered Trade Mark) which is a methylated reaction product of formaldehyde and allyl phenol.

Preparation of Electropaint

50 parts of component A, 50 parts of component B and 10 parts of component C were mixed together with vigorous stirring while 17.5 parts of triethylamine dissolved in 50 parts of demineralised water was added. Finally, 135 parts of demineralised water was added to give a dispersion having a 30 per cent solids content.

60 200 parts of iron oxide pigment and 100 parts of the 30 per cent solids dispersion were ground to a smooth paste in a ball-mill. A further 3,200 parts of the 30 per cent dispersion and 10,700 parts of demineralised water were added to give a final electropaint having a 10 per cent solids content.

65 Electropainting

The rupture voltage of the electropaint was 400 volts; it had very good throwing power. When the 50 parts of component A in the electropaint was replaced by a further 50 parts of component B, the rupture voltage was 180 volts.

70 Example 3.
Component A — Polybutadiene-Maleic Anhydride Product

75 100 parts of a polybutadiene having a viscosity of 7 poises at 25°C and 25 parts of maleic anhydride were heated at 190°C together with 3 parts of xylene and 0.3 part of an antioxidant (as in Example 2) until a

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	a trace of triethylamine were then added, and the mixture was held at 120°C for 40 minutes to hydrolyse the anhydride groups. Excess butanol was removed in a stream of nitrogen.	Component C
5	Component B — Polybutadiene-Maleic Anhydride Product	This was the p-octyl phenol-formaldehyde product used in Example 3.
10	100 parts of the polybutadiene used in component A and 5.25 parts of maleic anhydride were heated at 240°C with an antioxidant and a xylene reflux as for component A above until a viscosity of 5,000 poises at 25°C was achieved. The cooled resin was reduced to 85 per cent solids with xylene.	Preparation of Electropaint
15	Component C — Phenolic Resin	This was the same as that described in Example 3 except that, instead of 100 parts of the single component B(i) used therein, 50 parts of component B(i) and 50 parts of component B(ii) were used with 22 parts of triethylamine.
20	Preparation of Electropaint	Electropainting
25	100 parts of component A was heated at 120°C with 10 parts of component C for one hour. The cooled product was mixed with 100 parts of solid component B and 100 parts of a pigment pack comprising 50 parts of the pigment mixture of Example 1 dispersed in 50 parts of maleinised linseed oil. 20 parts of triethylamine were immediately added, followed by 2,000 parts of water to produce the desired electropaint.	The rupture voltage was 285 volts compared with less than 200 volts in the absence of component C.
30	Electropainting	Example 6.
35	Deposited on mild steel panels, the system ruptured at 270 volts. When component C was omitted the system ruptured below 180 volts.	In this Example, the component C used in Example 5 was replaced by the p-tertiary butyl phenol-formaldehyde product used in Example 4, the recipe and procedure being otherwise the same.
40	Example 4.	The rupture voltage in this case was 250 volts.
45	The recipe and methods of procedure were as set out in Example 3 with the single exception that the phenolic resin used was the commercially available reaction product of p-tertiary butyl phenol and formaldehyde (Super Beckacite 1001 ex Synthetic Resins Ltd.—BECKACITE is a Registered Trade Mark). The rupture voltage in this case was 240 volts.	Example 7.
50	Component A	Component A
55	Was the same as that used in Examples 3 and 4.	This was the same as that used in Example 1.
	Component B	Component B
	In this Example, a mixture of components B was used. The first, B(i), was the same as that set out in Example 3. B(ii) was prepared in the same manner set out in Example 3 using 100 parts of the polybutadiene and 11 parts of maleic anhydride reacted to a viscosity of 10,000 poises at 25°C.	This was also the same as that used in Example 1.
		Component C — Phenolic Resin
		470 parts of phenol, 700 parts of salicylic acid and 600 parts of para-formaldehyde were heated together with 500 parts butanol for 2 hours at 60°C, 4 hours at 90°C and then under reflux for 1 hour in a flask fitted with a Dean and Stark separator. 1,200 parts of butanol were added and the resin solution allowed to cool.
		Preparation of Electropaint
		10 parts of titanium dioxide and 10 parts of china clay were finely dispersed in 100 parts of component A. 60 parts of component B were then added together with 50 parts of component C. The product was immediately dispersed in a solution of 20 parts of triethylamine in 300 parts of water. The composition was further diluted with 400 parts of water to give the electropaint.
		Electropainting
		The electropaint when electropainted onto mild steel was found to have a rupture voltage of 230 volts.
		WHAT WE CLAIM IS:—
		1. An aqueous electropaint the binder of

which is a partially or completely neutralised composition which prior to neutralisation contains at least one of each of the following three essential ingredients A, B and C:

5 A a polydiene reaction product which is
 (i) the reaction product of a polydiene resin (as hereinbefore defined) with from 4 to 30 *per cent* of its weight of an α,β -ethylenically unsaturated dicarboxylic acid,
 10 (ii) the reaction product of (i) which has been partially esterified with an alcohol containing 1 to 4 carbon atoms in the molecule, or
 15 (iii) the reaction product of a polydiene resin (as hereinbefore defined) with from 4 to 30 *per cent* of its weight of an α,β -ethylenically unsaturated dicarboxylic anhydride, in which the anhydride content of the product has been substantially hydrolysed to the acid, or has been substantially half-esterified with an alcohol containing 1 to 4 carbon atoms in the molecule, or has been substantially converted to a monoamide by reaction with ammonia, or a primary or secondary amine;

20 B the reaction product of a polydiene resin (as hereinbefore defined) with from 4 to 30 *per cent* of its weight of maleic anhydride or itaconic anhydride; and

25 C a heat-reactive phenol-formaldehyde resin, the acid value of the components A and B in total being at least 30 mg/KOH/gram.

30 2. An electropaint as claimed in claim 1 in which the polydiene used in both component A and component B is a homopolymer of butadiene.

35 3. An electropaint as claimed in claim 1 or 2 in which component A (i) is present and is the reaction product of a polydiene resin and maleic acid.

40 4. An electropaint as claimed in claim 1 or 2 in which component A (ii) is present and is a partially esterified reaction product of a polydiene resin and maleic acid.

45 5. An electropaint as claimed in claim 1 or 2 in which component A (iii) is present and is derived from the reaction product of a polydiene resin and maleic anhydride.

50 6. An electropaint as claimed in claim 5 in which component A (iii) is derived from the reaction product of a polydiene resin and

from 15 to 30 *per cent* of its weight of maleic anhydride. 55

7. An electropaint as claimed in any of the preceding claims in which component B is the reaction product of a polydiene resin and from 5 to 10 *per cent* of its weight of maleic anhydride. 60

8. An electropaint as claimed in any of the preceding claims in which components A and B are present in a weight ratio of from 1:4 to 4:1 and the proportion of component C is from 1 to 25 *per cent* by weight of the total weight of components A and B. 65

9. An electropaint as claimed in any of the preceding claims in which component C is an alcohol-modified phenol-formaldehyde resin. 70

10. An electropaint as claimed in any of the preceding claims in which component A and/or component B and/or component C is substantially as described in any of the foregoing Examples. 75

11. An electropaint as claimed in any of the preceding claims containing in addition to the binder a pigment and up to 20 *per cent* by weight based on the total weight of components A, B and C of one or more additives. 80

12. An electropaint as claimed in any of the preceding claims containing titanium dioxide, iron oxide, carbon black, talc, clay or a chromate as pigment. 85

13. An electropaint as claimed in claim 1 and substantially as described in any of the foregoing Examples. 90

14. A process for the production of an electropaint as claimed in any of claims 1 to 12 which comprises mixing components A, B and C as defined in claim 1, at least partially neutralising the composition and dispersing it in water. 95

15. A process as claimed in claim 14 in which component C is mixed or co-condensed with component B prior to blending the mixture or product with component A. 100

16. An electropaint when manufactured by a process as claimed in claim 14 or 15.

17. A method of painting a metal article which comprises electrodepositing on said article an electropaint as claimed in any of claims 1 to 13 or 16. 105

18. A coated metal article when obtained by a method as claimed in claim 17.

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